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A. K. Bolvako, assistant lecturer (BSTU);

A. A. Chernik, PhD (Chemistry), assistant professor (BSTU)

ELECTROCHEMICAL Cr (III) OXIDATION WITH DOPED PbO₂ ANODES

The electrochemical oxidation of Cr (III) is of great importance in many electrochemical productions. One of the most common anodic electrode materials for this process is PbO₂, due to its high corrosion resistance in acidic media at high anodic potentials. In this paper, the rate constants of the anodic reaction of oxygen transfer in Na₂SO₄ and H₂SO₄ solutions containing Cr³⁺ at the volume-doped electrodes based on PbO₂ were estimated by using a rotating disk electrode.

Introduction. Electrochemical oxidation of Cr (III) requires electrode materials with high corrosion resistance, as the process takes place in a highly acidic medium, and with considerable stability at high anodic potentials. In the anodic process, the O₂ formation always takes place, which reduces the current efficiency of the Cr (III) oxidation. Therefore, an important problem is the preparation of anodic materials with high corrosion resistance, which make possible the catalytic Cr (III) oxidation without significant increase in the O₂ formation rate [1].

Among the most promising electrode materials for the anodic Cr (III) oxidation the PbO₂-based anodes can be mentioned. Their ever-growing use is based on the high O₂ overpotential at them, their high conductivity, availability, and high mechanical durability and chemical resistance [2]. In addition, PbO₂-electrodes have high electrocatalytic activity due to adsorbed ·OH particles formed on their surface [3].

It was shown [4–7] that in the process of anodic deposition, some metals can be incorporated into the PbO₂ matrix in the form of various oxides. Such materials are called “doped PbO₂-electrodes”. The rate of the anodic oxygen transfer reaction can be significantly increased through the insertion of Fe, Co, Ni, Bi, etc. dopants into the PbO₂ structure.

Electrochemical synthesis of PbO₂ is preferably carried out from dilute Pb²⁺ solutions in the nitric acid medium [1, 4–7]. As this takes place, precious metals or platinized titanium are most commonly used as the basis metals. In articles [8–11], it was shown that the corrosion-resistant anodes with high catalytic activity can be synthesized from hydrofluoboric electrolytes on the graphite base.

The aim of this work was to evaluate the electrocatalytic activity of the PbO₂/SnO₂ composition during anodic Cr (III) oxidation.

Experimental. The tested PbO₂/SnO₂ samples were electrochemically deposited in galvanostatic mode according [8]. The lead plates were used as cathodes.

To perform polarization measurements, an IPC Pro-M potentiostat with a rotating disk electrode VED-06 and software package were used. The measurements were performed in a temperature-controlled standard three-electrode electrochemical cell at 20°C. The working electrode was the carbon-silica one with visible surface area of 0.06 cm².

The saturated silver-chloride electrode was used as the reference one. Positive and negative potential sweep ranges were chosen on the basis of the beginning of anodic O₂ formation and cathodic oxide coating dissolution, respectively.

The determination of a heterogeneous rate constant (k , cm/s) was performed with the use of Koutecky – Levich equation [6]:

$$\frac{1}{I/SC} = \frac{1}{nkF} + \left(\frac{1}{0.62nD^{2/3}\nu^{-1/6}} \right) \left(\frac{1}{\omega^{1/2}} \right),$$

where I – current, A; S – the disk surface area, cm²; C – volume concentration of the reagent, mol/cm³; n – effective number of the electrode process electrons; F – Faraday constant, equal to 96.480 C/mol-eq; D – effective diffusion coefficient of the reagent, cm²/s; ν – kinematic viscosity of the solution, cm²/s; ω – rotational speed, rad/s.

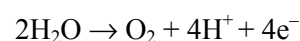
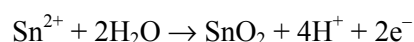
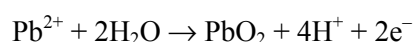
I values were measured at a constant potential and adjusted for the value of the background current. The values of D and ν are taken from [12].

To prepare all the solutions, the reagents of the “chemically pure” and “analytical grade” grades and distilled water were used.

Results and discussion. Electrodeposition of the coating samples was carried out at the current density of 1 A/dm² during the time required to obtain a coating with the thickness of up to 50 μm at a rotation speed of the working electrode of 1,000 rev/min.

Chronopotentiometric curve obtained at the electrodeposition step (Fig. 1) is in good agreement with the data [6]. Maximum point on the curve, which was observed during the first 100 s, can be caused by crystallization overpotential of the new phase formation. Subsequently, the electrodeposition potential value stabilized at about 1.8 V and remained almost unchanged throughout the process of the active coating formation.

During the electrochemical synthesis of PbO₂/SnO₂ composition the following processes take place:



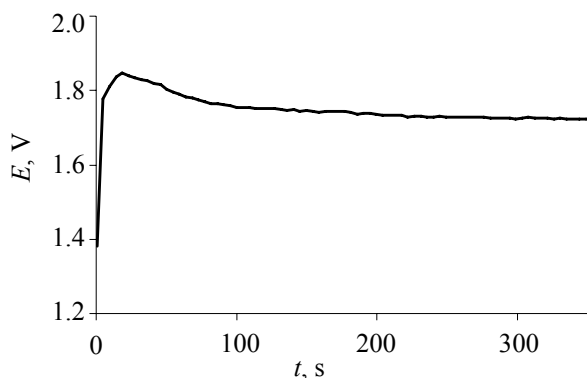


Fig. 1. The anode potential gradient during the PbO₂/SnO₂ deposition

As it was shown earlier [8, 9, 11], under these conditions, the formation of anode composite coating containing up to 3.5 at. % Sn takes place. The coating formed has an oxygen deficit, and due to the use of the hydrofluoboric electrolyte, up to 1.86 at. % of fluorine is incorporated into PbO₂ composition, which can also help to increase the catalytic activity of the coating. The presence of oxygen-containing particles and adsorbed water on the surface of the oxide electrode has a great importance in the electrocatalysis process at high positive potentials [4].

The coatings synthesized in such a manner were used for electrochemical Cr (III) oxidation in a medium of 0.5 M of H₂SO₄ and 0.5 M of Na₂SO₄. Cyclic current-voltage curves (CCV) obtained at the PbO₂/SnO₂-electrode ($\omega = 2,000$ rev/min, potential sweep rate – 50 mV/s, Cr (III) concentration – 1 mmol/dm³) in 0.5 M H₂SO₄ solution is of the form shown in Fig. 2. Based on Fig. 2, the presence of Cr (III) in solution results in the current increase at the direct and reverse run of the CCV-curve, which may indicate the electrochemical process involving Cr (III) ions.

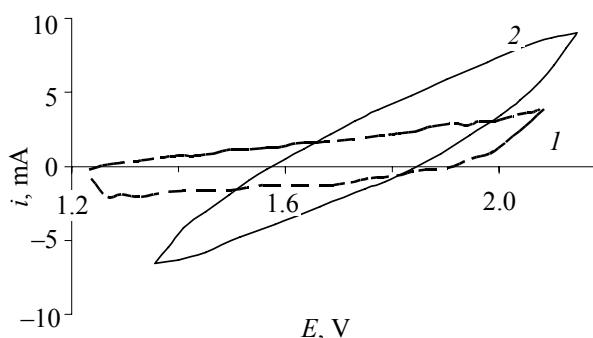


Fig. 2. CCV-curves:
1 – 0.5 M H₂SO₄;
2 – 0.5 M H₂SO₄ + 10⁻³ M Cr (III)

Based on the CVV-curves data for different solutions containing 1 mmol/dm³ of Cr (III) the catalytic activity of the PbO₂/SnO₂ coating during the

Cr (III) oxidation was evaluated. To determine the catalytic activity at 1.8, 1.9 and 2.0 V potentials, partial Cr (III) electrooxidation current values were calculated as the difference between the current value in a solution containing Cr (III), and the amount of current in the background electrolyte. The values obtained were processed in the Koutecky – Levich coordinates. Fig. 3 shows the $(I/SC)^{-1} = f(\omega^{-1/2})$ functions for the 0.5 M sulfuric acid solution.

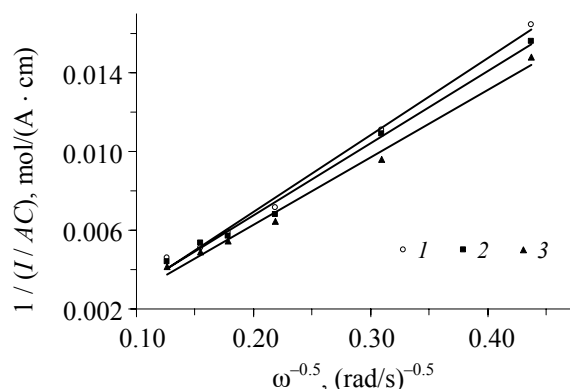


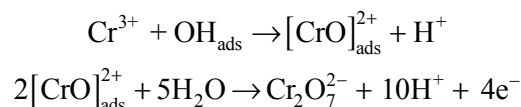
Fig. 3. Koutecky – Levich plots for PbO₂/SnO₂ in a solution of 0.5 M H₂SO₄ + 10⁻³ M Cr (III) at potentials:
1 – 1.8 V; 2 – 1.9 V; 3 – 2.0 V

Based on Fig. 2, in the potential range of 1.8–3.0 V, there is some variation of the rate constant of the anodic process.

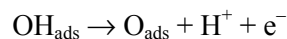
It can be assumed that the Cr (III) oxidation is a multi-step process that involves interaction with the oxygen particles chemisorbed on the surface of the electrode. At the anodic polarization on the PbO₂ surface, the OH_{ads} formation takes place:



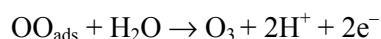
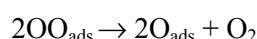
OH_{ads} interaction with Cr (III) ions in accordance with the chemical mechanism can lead to the formation of the adsorbed product, which is subsequently oxidized to Cr (VI) [3]:



At that, within the potential range of 1.6–1.9 V, the increase in the number of OH_{ads} should contribute to the increase of the rate of the [CrO]_{ads}²⁺ intermediate product formation and with the further increase of the potential, OH_{ads} will be used for the reaction of the formation of adsorbed O_{ads} particles:



that are further used for the oxygen formation, and with the anodic potential increase – for a ever increasing amount of ozone [10]:



The values of the anodic process rate constants for the electrolytes studied at a Cr (III) concentration of 1 mmol/dm³, depending on the anode potential value E , are given in the following Table.

The constants of Cr (III) oxidation rate

Electrolyte	E , V	$k \cdot 10^3$, cm/s
0.5 M Na ₂ SO ₄ , pH = 2.3	1.8	39 ± 1.0
0.5 M H ₂ SO ₄	1.8	18 ± 0.6
	1.9	19 ± 0.6
	2.0	17 ± 0.6

Conclusion. It was found that the doped electrodes based on PbO₂ have rather a high electrocatalytic activity during process of the Cr (III) oxidation in sulfuric acid solutions.

References

1. Cr (III) oxidation with lead dioxide-based anodes / D. Devilliers [et al.] // *Electrochimica Acta*. – 2003. – Vol. 48. – P. 4301–4309.
2. Коровин, Н. В. Электрокатализаторы электрохимических устройств / Н. В. Коровин, Э. В. Касаткин // *Электрохимия*. – 1993. – Т. 29, № 4. – С. 448–460.
3. Danilov, F. I. Electrocatalytic activity of anodes in reference to Cr (III) oxidation reaction / F. I. Danilov, A. B. Velichenko // *Electrochimica Acta*. – 1993. – Vol. 38. – P. 437–440.
4. Mohd, Y. The influence of deposition conditions and dopant ions on the structure, activity and stability of lead dioxide anode coatings / Y. Mohd, D. Pletcher // *Journal of The Electrochemical Society*. – 2005. – Vol. 152. – P. D97–D102.
5. Electrosynthesis and physicochemical properties of Fe-doped lead dioxide electrocatalyst / A. B. Velichenko [et al.] // *Electrochimica Acta*. – 2000. – Vol. 45. – P. 4341–4350.
6. Electrodeposition of Co-doped lead dioxide and its physicochemical properties / A. B. Velichenko [et al.] // *Journal of Electroanalytical Chemistry*. – 2002. – Vol. 527. – P. 56–64.
7. Comparison of voltammetric responses of toluene and xylenes at iron (III)-doped, bismuth (V)-doped, and undoped β -lead dioxide film electrodes in 0.50 M H₂SO₄ / S. E. Treimer [et al.] // *Journal of The Electrochemical Society*. – 2001. – Vol. 148, № 12. – P. E459–E463.
8. Болвако, А. К. Электрохимический синтез анодов на основе композиции PbO₂/SnO₂ / А. К. Болвако, А. А. Черник, И. М. Жарский // *Вест. Нац. акад. наук Беларуси. Сер. хим. наук*. – 2010. – № 4. – С. 50–54.
9. Болвако, А. К. Получение PbO₂-SnO₂ анодов и их применение для электрохимического синтеза озона / А. К. Болвако, А. А. Черник, И. М. Жарский // *Свиридовские чтения: сб. ст.* – Минск, 2008. – Вып. 4. – С. 199–204.
10. Болвако, А. К. Электрохимическое поведение PbO₂/SnO₂ в сернокислых электролитах / А. К. Болвако, А. А. Черник, И. М. Жарский // *Свиридовские чтения: сб. ст.* – Минск, 2009. – Вып. 5. – С. 166–174.
11. Болвако, А. К. Электрохимический синтез и свойства анодов на основе композиции PbO₂/SnO₂, допированной Co²⁺ / А. К. Болвако, А. А. Черник, И. М. Жарский // *Молодежь в науке – 2009: прил. к журн. «Весті Нацыянальнай акадэміі навук Беларусі»*. В 5 ч. Ч. 1. Серия химических наук / редкол. Н. П. Крутько (гл. ред.) [и др.]. – Минск: Беларус. навука, 2010. – С. 13–16.
12. Волков, А. И. Большой химический справочник / А. И. Волков, И. М. Жарский. – Минск: Современная школа, 2005. – 608 с.

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